THE CATALYTIC HYDROGENATION OF QUINOLINE

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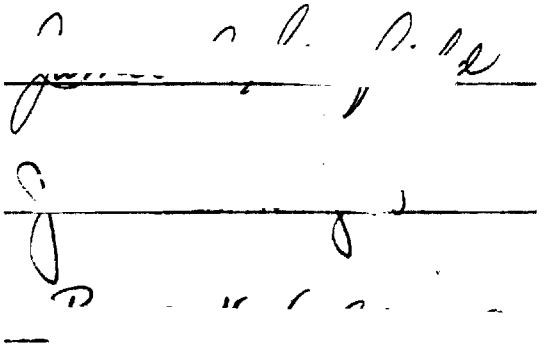

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ABSTRACT

A study has been made of the kinetics of the catalytic hydrogenation of quinoline. Adams' platinum catalyst was employed in acetic acid medium under an initial hydrogen pressure of 64 pounds per square inch. A standard Parr Hydrogenation Apparatus was used.

Quinoline hydrogenates to tetrahydroquinoline as a one-step process in the temperature range 17 - 37° C. The rate of hydrogenation is zero order with respect to concentration of hydrogen acceptor, first order with respect to hydrogen pressure and directly proportional to the amount of catalyst used. On the basis of these results a mechanism is proposed for the hydrogenation of quinoline to tetrahydroquinoline.

The rate constant of the process has been determined to be 142×10^{-4} reciprocal minutes with a catalyst that would hydrogenate benzoic acid under identical conditions at a rate of 193×10^{-4} reciprocal minutes in a system whose volume was 4.43 liters. However, it is shown that benzoic acid is not suitable as a catalyst standard to correlate rates of hydrogenation determined with different catalysts. These rates show a wide variation. It is shown further that purity of the quinoline is of prime importance, it being necessary to keep the quinoline under an atmosphere of nitrogen to obtain consistent results.

A limited amount of additional work indicates that quinoline may hydrogenate by a different mechanism at higher temperatures. Some experimental evidence indicates that tetrahydroquinoline probably hydrogenates to decahydroquinoline at a rate of $60. \times 10^{-4}$ reciprocal minutes, although catalyst poisoning interfered somewhat with an accurate determination of this rate.

THE CATALYTIC HYDROGENATION OF QUINOLINE

I. INTRODUCTION

Catalytic hydrogenation, especially with Ni, Cu-Cr, and Pt catalysts, has become an invaluable process in the industrial production of pure and technical products, in the laboratory synthesis of important chemicals, and in the study of reaction kinetics through reaction rates and mechanisms.

Of these catalytic materials Pt in the form of platinum black and colloidal platinum was one of the earliest to find widespread application.[1,2] Later, a catalyst consisting essentially of PtO_2 was found by Adams and co-workers to have ability to bring about the reduction of compounds more readily than other catalysts.[3] It proved to be particularly suitable for overcoming the characteristic unreactivity associated with aromaticity when employed at room temperature with 3-4 atmospheres pressure of hydrogen in glacial acetic acid as solvent for the material to be hydrogenated.[4,5]

Although research of a qualitative nature was conducted with platinum and with other metallic catalysts reasonably early, little was

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[1] R. Willstatter and D. Hatt, Ber. 45, 1471 (1912).

[2] A. Skita and W. A. Meyer, Ber. 45, 3589 (1912).

[3] V. Voorhees and R. Adams, J. Am. Chem. Soc., 44, 1397 (1922).

[4] R. L. Shriner and R. Adams, J. Am. Chem. Soc., 45, 2171 (1923).

[5] R. Adams and J. Marshall, J. Am. Chem. Soc., 50, 1970 (1928).

attempted in quantitative study of reaction rates before 1945. At that time a study of this kind on the kinetics of the catalytic hydrogenation of the benzene nucleus was begun by H. A. Smith and co-workers. They employed Adams' Platinum Catalyst for the reduction of phenyl-substituted aliphatic acids, benzene, alkyl benzenes, and polymethylbenzenes, under essentially the same conditions used by Adams and co-workers.

From these studies on the hydrogenation of the benzene nucleus, Smith et al have concluded that:

1. The reaction is zero order with respect to the concentration of the compound being hydrogenated;
2. The rate is directly proportional to the amount of catalyst used;
3. The reaction rate is first order with respect to hydrogen pressure;
4. The phenyl group is strongly adsorbed on the catalyst while the other portions of the molecule are not;
5. Resonance is not a factor which influences greatly the reaction rate;
6. The symmetry of the molecule is an important factor in determining the reaction rate.[6,7,8,9]

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[6]H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., 67, 272 (1945).

[7]H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 67, 276 (1945).

[8]H. A. Smith and H. T. Meriwether, J. Am. Chem. Soc., 71, 413 (1949).

[9]H. A. Smith and J. A. Stanfield, J. Am. Chem. Soc., 71, 81 (1949).

In one of the more recent phases of this study Smith and Stanfield extended the investigation to the pyridine nucleus. Again the rate of hydrogenation was found to be directly proportional to the amount of catalyst, and symmetry in the molecule played an important role in governing the rate of reduction. However, certain modifications in some of the other conclusions were found necessary:

1. Increasing the concentration of pyridine was found to decrease the rate slightly;
2. True first order dependence of the rate on hydrogen pressure was observed only with the small changes in pressure of a single hydrogenation run. An order of 0.98 was calculated over larger pressure drops.

In addition, it was found that position of a substituent relative to the N atom affected the reaction rate. Alpha greater than beta greater than gamma was the order of ease of hydrogenation. Finally, determination of the activation energy of the hydrogenation resulted in two values: 10,500 calories per mole for the range 15 - 23° C, and 4500 calories per mole for the range 23 - 45° C.[10]

The purpose of the present investigation has been to test the applicability of the conclusions drawn on the hydrogenation of the benzene and pyridine nuclei separately, to the case in which the nuclei are combined - the quinoline molecule. Quinoline has been catalytically reduced to tetrahydroquinoline with Ni[11] and with Cu-Cr,[12] and to the

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[10]J. A. Stanfield, "Kinetics of Catalytic Hydrogenation," Doctoral Dissertation, University of Tennessee, 1947, pp. 74-104.

[11]F. F. Diworky and H. Adkins, J. Am. Chem. Soc., 53, 1868-75 (1931).

[12]R. Conner and H. Adkins, J. Am. Chem. Soc., 53, 1091 (1931).

tetrahydro- and decahydro-compounds with PtO_2.[13] In each case, however, the approach was qualitative rather than kinetic. This investigation is a study of the kinetics of the hydrogenation of quinoline, the factors influencing the rate of reduction and an interpretation of the mechanism. No such study has previously been made.

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[13] J. Overhoff and J. P. Wibaut, Rec. Trav. Chim., 50, 957-80 (1931).

II. THEORETICAL DISCUSSION

This investigation has been designated a study of the kinetics of the catalytic hydrogenation of quinoline. The term "kinetics," however, is generally but vaguely defined. Hammett[1] and Getman and Daniels[2] imply by this term a consideration both of reaction rate and reaction mechanism. In this work, however, a somewhat more general definition of "chemical kinetics" will be assumed: a consideration of the process of passing from reactants to products under specified conditions. Such a study should cover reaction rate, factors influencing the rate, possible reaction mechanism, energies involved, and correlation with similar reactions. A theoretical discussion of catalytic hydrogenation should treat, in addition to kinetics, certain aspects of heterogeneous catalysis. Adsorption, activation, deactivation, and selectivity as applied to catalysis will be considered.

A. Chemical Kinetics

1. Reaction Rates.

Hammett points out that "the basic assumption of all reaction rate investigations is the principle that the rate of a reaction, i.e., the number of moles reacting in unit time, is proportional to the product of the concentrations of the reacting substances and independent of the concentrations of substances that do not take part in the reaction,

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[1]L. P. Hammett, Physical Organic Chemistry (New York and London: McGraw-Hill Book Co., Inc., 1940), pp. 96-7.

[2]F. H. Getman and F. Daniels, Outlines of Physical Chemistry, 7th Edition, (New York: John Wiley and Sons, Inc., 1945), pp. 342, 584.

provided that the medium in which the reaction occurs is reasonably constant."[3] This principle is certainly reasonable from the standpoint of collision and transition state theories of reaction mechanism. In addition, it is amply verified experimentally in many reactions and leads to valuable results even in those cases of apparent exceptions.

In attempting to express this relation of reaction rate to concentration in a mathematical form it has been found useful to define a term "order of reaction." The order of a reaction with respect to a reactant indicates the exponent to which the concentration of the reactant must be raised in the expression for the reaction rate. Thus, for a reaction whose mechanism could be expressed by:

$$2\,A + B = C, \tag{1}$$

the rate of disappearance of A, $-\frac{dc}{dt}$,

$$-\frac{dc}{dt} = (k)\,(A)\,(A)\,(B). \tag{2}$$

This implies that the reaction is second order with respect to (A) and first order with respect to (B). Overall, the reaction is third order, since the overall order of a reaction indicates the total number of concentration factors appearing on the right hand side.

The proportionality constant in (2) above, k, is called the "specific reaction rate constant," or simply the "rate constant" of the reaction. Mathematically and physically, this is seen to be the rate of the reaction when all reactants are at unit concentration. Actually

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[3]L. P. Hammett, op. cit., p. 96.

this "constant" is essentially invariant only with concentration. Temperature has a very definite effect upon it, as shall be discussed later. Traces of impurities profoundly alter the values for this "constant" obtained experimentally.

To evaluate this constant experimentally it is convenient to use the integrated forms of equations similar to (2). Integration of such equations is performed easily only in the simple cases of zero and first order dependence of rate upon concentration. However, it is only with these two that the present work is concerned.

For zero order dependence the expression may be derived as follows:

$$-\frac{dc}{dt} = k \tag{3}$$

$$-\int_{c_1}^{c_2} dc = k \int_{t_1}^{t_2} dt \tag{4}$$

$$c_2 - c_1 = -k\,(t_2 - t_1). \tag{5}$$

In a similar fashion for first order dependence:

$$-\frac{dc}{dt} = k\,c \tag{6}$$

$$-\int_{c_1}^{c_2} \frac{dc}{c} = k \int_{t_1}^{t_2} dt \tag{7}$$

$$\ln \frac{c_2}{c_1} = - k (t_2 - t_1) \qquad (8)$$

$$\log \frac{c_2}{c_1} = - \frac{k}{2.303} (t_2 - t_1) \qquad (9)$$

Equations (5) and (9), which apply to a general case, may be made simpler and more useful for the present work by replacing c_1 by c_o, the initial concentration; c_2 by c, the final concentration; t_1 by 0, the initial time; t_2 by t, the final time. Thus we obtain:

$$c - c_o = k t \qquad (10)$$

and

$$\log \frac{c}{c_o} = - \frac{kt}{2.303} . \qquad (11)$$

Finally, for a gaseous reactant, in which case

$$\frac{c}{c_o} = \frac{p}{p_o} , \qquad (12)$$

p_o being the initial pressure and p being the final pressure, the first order rate equation becomes:

$$\log \frac{p}{p_o} = - \frac{kt}{2.303} .^4 \qquad (13)$$

According to equation (10), for a reaction which is zero order with respect to a reactant c, the decrease in concentration of c is a linear function of the time. Such a zero order dependence was observed

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[4]F. H. Getman and F. Daniels, op. cit., pp. 345-353.

by Smith and co-workers when studying the effect of concentration of hydrogen acceptor upon the rate of hydrogenation in the benzene series.[5] The first order equation (13) indicates a linear relation between the logarithm of the initial over the final concentration and the time. The rate of hydrogenation of the benzene nucleus was found to be first order with respect to hydrogen pressure.[5]

2. Factors Influencing the Reaction Rate Constant.

From the definition of reaction rate constant as the proportionality constant in equation (2) above, and from general considerations of the means whereby molecules are believed to react, it should be expected that this "constant" would vary with such factors as temperature, hydrogen volume, and nature of the interacting substances. The interacting substances in this work are taken to be hydrogen, quinolinium ion, and platinum catalyst. Also, it is conceivable on the basis of studies of concentrated solutions and of statistical mechanics that the proportionality factor might not remain constant at very large and small concentrations of reactants. Consideration will be given to each of these variables in regard to their effect upon the measured values of the reaction rate constant.

a. Temperature. Of prime importance in the kinetics of catalytic hydrogenation is the effect of temperature upon reaction rate. A doubling of the rate for each ten degree rise in temperature is frequently good to a first approximation. A more nearly quantitative study of this

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[5]H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 67, 279 (1945).

variable has been made by attributing changes in reaction rate to changes in the reaction rate constant, k.

Arrhenius was the first to propose a relation between rate constant and temperature. He observed a logarithmic relation which may be expressed:

$$\ln k = \frac{a}{T} + b, \tag{14}$$

T being the absolute temperature and a and b being experimentally determined constants. When differentiated this becomes:

$$\frac{d \ln k}{dT} = -\frac{a}{T^2} . \tag{15}$$

In an attempt to attribute some physical significance to the factor "a" in equation (15), reference is made to the expression ordinarily written for the dependence of an equilibrium constant upon temperature:

$$\frac{d \ln K}{dT} = \frac{H_f - H_i}{R T^2} ,^{6} \tag{16}$$

where K is an equilibrium constant, $H_f - H_i$ the change in heat content during the reaction, and R the universal gas constant. By a purely formal analogy equation (15) may be rewritten:

$$\frac{d \ln k}{dT} = \frac{E_a}{R T^2} , \tag{17}$$

which, when integrated and converted to base-ten logarithms, becomes:

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[6]F. H. Getman and F. Daniels, op. cit., p. 295.

$$\log k = -\frac{E_a}{2.303\ R\ T} + C_1. \qquad (18)$$

The letters k, R, and T in equations (17) and (18) have their usual significance, and C_1 is a constant of integration. The quantity E_a may be considered defined by either of these equations. It is usually given the interpretation of "heat of activation" or "energy of activation" by comparison with equation (16).

An expression for the relation of rate constant to temperature may be derived by theoretical considerations of the collision theory of reaction mechanism. It may be expressed:

$$\frac{d \ln k}{dT} = \frac{1}{2\ T} + \frac{E}{R\ T^2}. \qquad (19)$$

Since the rate constants in equations (17) and (19) must be the same, it must follow that

$$E_a = E + \frac{1}{2} R\ T. \qquad (20)$$

In general, however, because of the difficulty encountered in evaluating it accurately, E_a is not known to a precision which justifies considering the small correction term, $\frac{1}{2} R\ T$. Equation (19) then becomes identical to equation (17), and Arrhenius's empirical relation is seen to have some theoretical backing.[7]

By equation (18) a plot of log k as a function of $\frac{1}{T}$ would give a straight line the slop of which would equal $-\frac{E_a}{2.303\ R}$. Therefore,

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[7]L. P. Hammett, op. cit., pp. 111-114.

by multiplying the slope of the line determined from the plot by 2.303 R, a value is obtained for the energy of activation, E_a.

Should some fundamental change occur in the reaction mechanism in going from lower to higher temperatures, a change of slope would likely occur for the line representing the dependence of log k upon $\frac{1}{T}$. According to Hinshelwood, "This is an almost certain indication that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature."[8] He further points out that an effect of temperature upon the fraction of catalyst surface covered with reactants, upon the energy of adsorption of reactants on the catalyst surface, and upon similar factors would in general result in a change of slope and thus in a change in the activation energy.[9] The existence of two activation energies was observed in the case of pyridine and methyl-substituted pyridines.[10]

Activation energy or energies as obtained above for a given reaction are of considerable interest from a theoretical standpoint. They provide a quantitative means of comparing two reactions over the same temperature range. However, from a practical standpoint the energy of activation is even more useful in converting rate constants at one temperature to any other temperature within the range over which the activation energy applies.

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[8]C. N. Hinshelwood, The Kinetics of Chemical Change (Oxford: Oxford University Press, 1940), p. 45.

[9]Ibid., pp. 216-217.

[10]J. A. Stanfield, "Kinetics of Catalytic Hydrogenation," Doctoral Dissertation, University of Tennessee, 1947, pp. 84-88.

For this purpose, equation (17) may be integrated as follows:

$$\int_{k_1}^{k_2} d \ln k = \frac{E_a}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} . \qquad (21)$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) . \qquad (22)$$

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303\ R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) . \qquad (23)$$

If values are known for E_a and for k_1 at temperature T_1, a value for k_2 at temperature T_2 may easily be calculated.

A useful plot is obtained from equation (23) by calculating from it $\Delta \log k$ at a series of temperatures, taking T_1 equal to T and T_2 equal to $T + \Delta T$, where ΔT is an arbitrary unit, e.g., one degree. Plotting $\Delta \log k$ against T gives a curve from which the rate of change of log k with temperature, $\frac{\Delta \log k}{T}$, may be read directly at any given temperature T.

b. Volume. The effect of temperature upon rate of reaction and thus upon the reaction rate constant is familiar to all chemists. However, the effect of volume of gaseous reactant upon the observed value of the reaction rate constant is somewhat less familiar.[11] This effect may be shown quite easily by considering two reactions involving a gaseous

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[11] J. F. Fuzek and H. A. Smith, "Kinetics of Heterogeneous Reactions with Special Reference to Catalytic Hydrogenation," J. Am. Chem. Soc., 70, 3743 (1948).

reactant, e.g., hydrogen.

For simplicity it is assumed that the gas acts ideally and that each reaction occurs at constant volume, at the same temperature and at the same initial pressure. The decrease in energy associated with the reactions may be expressed by equations (24) and (25):

$$P_1 V_1 - P^o V_1 = n_1 R T - n_1^o R T \qquad (24)$$

$$P_2 V_2 - P^o V_2 = n_2 R T - n_2^o R T, \qquad (25)$$

where P^o, n_1^o and n_2^o represent the initial states, and P_1, n_1, P_2 and n_2 represent the final states.

If the changes represented by equations (24) and (25) are considered as infinitesimal changes, these equations may be rewritten:

$$V_1 \, dP_1 = R T \, dn_1 \qquad (26)$$

$$V_2 \, dP_2 = R T \, dn_2. \qquad (27)$$

Furthermore, if reactions represented by equations (24) and (25) are permitted to proceed a time dt such that dn_1 is equal to dn_2, it follows that

$$V_1 \, dP_1 = V_2 \, dP_2. \qquad (28)$$

For a reaction that is first order with respect to the pressure of a reactant, its rate may be expressed:

$$-\frac{dp}{dt} = k p. \qquad (29)$$

At the time that P is equal to P^o, this equation takes the form:

$$dP_1 = - k_1 P^o dt \qquad (30)$$

$$dP_2 = - k_2 P^o dt \qquad (31)$$

for the two reactions represented by equations (24) and (25). Combining equations (28), (30), and (31):

$$V_1 k_1 = V_2 k_2, \qquad (32)$$

$$V \; k = \text{a constant.} \qquad (33)$$

The great significance of equation (33) is realized when it is noted that nearly all investigators in the field of reaction rates have failed to note the volume of the system they employed. Clearly, anyone repeating the work under the same conditions, with a system having a different volume, would not obtain the same value for the reaction rate constant.

3. Reaction Mechanism.

The ultimate goal of the organic chemist is to understand completely the processes occurring in all organic reactions, so that he may predict the factors of interest in any new reaction. The key to an understanding of any process is a knowledge of the mechanism whereby the process occurs. Hence, considerable attention is devoted in organic chemistry to the study of mechanisms.

The study of mechanisms is unfortunately a negative study. With few exceptions it is not possible to outline a mechanism theoretically or empirically and conclude without question that it is the correct one. Rather, a series of mechanisms must be considered. Then, on the basis of

the general principles of organic chemistry, of analogies to similar reactions, and of such experimental evidence as may be obtained, it is hoped that only one will be found to fit.

In most cases a number of mechanisms have been found to be based upon a single theory. Such theories are of great value in studying new reactions. However, new evidence discounting such theories does much to discount all mechanisms based upon them. Hence, no mechanism can be regarded as any more nearly correct than the theories which it presupposes. New and improved experiments may lead to new insight into a problem, and ultimately experiments must be the criterion.

To deduce a mechanism for a given reaction, groups of rate equations are formulated, based upon the substances observed to be present. By considering possible relative magnitudes of the rate constants of individual steps orders for the reaction are proposed. It is then necessary to determine experimentally the order of the reaction, overall and with respect to each reactant. Finally by comparing the observed order of the reaction with respect to each variable with that deduced from theory, the proposed mechanisms are either confirmed or denied. Such a study as this will be made for the hydrogenation of quinoline.

B. Catalytic Hydrogenation

The process of catalytic hydrogenation implies the union of a compound with hydrogen in the presence of a catalyst, a substance which alters the rate of a reaction but is not itself altered in the process.[12] If such a process occurs in a medium of only one phase, it is termed homogeneous catalysis, while if the catalyst is an insoluble, generally finely-divided material, the process is termed heterogeneous catalysis.

Adkins has listed a number of requirements for a so-called "good" catalyst: It should

1. be stable in the presence of the reactants;
2. adsorb and activate hydrogen;
3. adsorb and activate the hydrogen acceptor;
4. hold the activated hydrogen and hydrogen acceptor in the proper relationship for reaction;
5. desorb or set free the reaction products.[13]

It is significant to note from a mechanism standpoint that Adkins considers both the hydrogen and hydrogen acceptor are adsorbed on the catalyst.

To obtain a complete picture of the reaction utilizing such a catalyst, several phases will be considered; namely, adsorption and desorption, promotion, poisoning, and selectivity.

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[12] F. H. Getman and F. Daniels, op. cit., p. 398.

[13] H. Adkins, Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts (Madison: The University Press, 1937), p. 9.

1. Adsorption.

Inherent in the action of a catalyst in a heterogeneous process is the adsorption and activation of the reactants on the catalyst surface and the desorption of the products from it. Considerable study has been given these processes, and some interpretations of considerable interest have resulted.

Attempts have been made to classify adsorption phenomena into groups and to treat these separately. Thus, Lohse considers three classes:

1. Physical adsorption by secondary valences (so-called van der Waals' adsorption), comprising, e.g., adsorption of gases by solids at low temperatures;
2. "Activated" adsorption, occurring at higher temperatures than (1.);
3. "Chemisorption," associated with the formation of chemical bonds.[14]

Such classifications are useful in comparing and contrasting various phenomena, but here, as in many other cases, the problem of distinguishing among valence, van der Waals' forces, natural and activated states, and the like is more than can be handled in a simple fashion.

Although a rigid classification of adsorption phenomena cannot easily be made, an overall picture of the adsorption process can be made, correlating it with recent advances in the study of chemical bonding. It has been proposed[15] that adsorption of material, such as a benzene

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[14]H. W. Lohse, Catalytic Chemistry (Brooklyn, New York: Chemical Publishing Co., 1945), p. 83.

[15]W. H. Eberhardt, Georgia Institute of Technology, Private Communication.

nucleus, on a catalytic surface such as platinum is associated with an overlapping of the "p orbitals" of the carbon atoms in the benzene ring with the orbitals of the metallic atoms projecting above the surface of the catalyst. Pauling has correlated the extent of overlapping of such orbitals with the strength of the bonds formed.[16]

Of considerable importance, necessarily, is the relative distances between atoms both in the metallic and in the adsorbed substances. Comparisons using crystal lattice distances for platinum and C - C distances for benzene obtained through X-ray diffraction studies show that the meta and para positions in benzene coincide directly with the platinum atoms for certain lattice planes in the platinum.

This interpretation of the adsorption phenomenon is limited in that at present experiments have not been devised whereby it may be rendered more nearly quantitative and may be used as a basis for calculations. It is valuable, however, since it provides a reasonable interpretation of many experimental facts. It is known, for example, that at low temperatures platinum acts as a hydrogenation catalyst, while at high temperatures it acts as a dehydrogenation catalyst.[17] In terms of this interpretation it would be concluded that the change in bond distance with temperature for the metallic material differs from that of the adsorbate. Similarly, regarding desorption, this interpretation would state merely that, as a result of the chemical reaction taking place,

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[16]L. Pauling, The Nature of the Chemical Bond (Ithaca, N.Y.: Cornell University Press, 1945), p. 76.

[17]H. W. Lohse, op. cit., pp. 204, 219.

the orbitals of the material to be hydrogenated which were involved in the adsorption were no longer available.

In addition to such proposals and interpretations as that discussed, some theoretical work of interest has been developed for quantitative and semi-quantitative studies. Thus, semi-quantitative estimates of the relation of such factors as pressure to the extent of adsorption of gases on solids such as a catalytic surface have been made. Langmuir, on the basis of considerable experimental data formulated an adsorption isotherm, useful in the study of gaseous adsorption. It may be expressed in the form:

$$F = \frac{a\,u}{v + a\,u} \tag{34}$$

where F denotes the fraction of the contact surface covered with gas molecules at any moment, a is the fraction of the total number of molecules striking the surface in a unit time, v is a constant for a given gas and surface. u is given by

$$u = \frac{43.74\,p}{M\,T^{\frac{1}{2}}} \tag{35}$$

p being the total pressure, M the molecular weight, and T the absolute temperature.[18]

General expressions such as the Langmuir isotherm are few and their applicability limited. The lack of such expressions is acutely

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[18]H. B. Weiser, Colloid Chemistry (New York: John Wiley and Sons, Inc., 1946), p. 51.

felt when the subject of "activated" adsorption is considered. In order for the term to have any meaning it is necessary to accept some definition. Lohse defines this term as adsorption occurring at relatively high temperatures that may be reversed by reducing the pressure.[19] Such a definition gives no clear picture of the actual state of such a condition nor its usefulness in catalytic investigations. This vagueness in the actual meanings of terms is common in the field of adsorption to a larger extent than in many other fields. This is perhaps true since adsorption is intimately connected with catalyst surfaces, poisons, promoters, and other involved subjects.

2. Promoters and Poisons.

Platinum oxide, Raney nickel, and copper-chromium oxide are capable of influencing the rate of chemical reactions when present in relatively small amounts. Substances with this common property have been designated as catalysts. There are a variety of materials, however, which when present in a catalyst in merely trace quantities are capable of influencing to a considerable extent the action of the catalyst. These materials fall into two general classes depending upon whether theirs is a positive or negative effect upon the action of the catalyst. Attention should be called to the difference between the action of these trace materials and that of "supports" sometimes employed in catalytic work.

For clarity, these terms may be defined as follows: "A 'promoter' is a substance which, in itself, may possess but slight catalytic activity

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[19]H. W. Lohse, op. cit., pp. 87-8.

but which materially increases the activity of the catalyst to which it is added in relatively small amounts. If two substances are present in more or less equal quantities, the resulting product is called a 'mixed catalyst;' if the non-catalytic material is in large excess, it is designated as a 'catalyst support.'[20] The term 'poison' in contact catalysis is applied to anything that cuts down the velocity of a given catalytic reaction."[21]

a. Promoters. Weiser summarizes the assumptions and proposals made for promoter action, which in effect increases or modifies the surface of the catalyst. A promoter may

1. act by increasing the number of active centers as a result of an increase in the number of crystal faces, edges, and corners on the catalytic surface;
2. furnish an interface at which adsorption takes place;
3. increase the velocity of activated adsorption;
4. change the ratio of adsorption of two reacting substances;
5. activate one of the reacting substances which the catalyst did not activate appreciably;
6. decrease the stability of an intermediate product;
7. decrease the adsorption of one of the products below the point at which it has a poisoning action;
8. modify the nature of the orientation of the catalyst crystals.

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[20] H. B. Weiser, op. cit., p. 358.

[21] Ibid., p. 354.

b. Poisoning. Since a heterogeneous catalytic reaction takes place at a surface, a poison is anything which decreases the rate at which reacting substances reach the surface, or which prevent them from reaching it. The catalyst poison may be any substance that is adsorbed more strongly on the catalytic surface than the reactants. In particular it may be a reaction product adsorbed too strongly to be removed easily (autotoxic catalysis). Although it frequently causes considerable difficulty, poisoning is not per se an undesirable effect. Considerable evidence has been offered in support of the idea that poisoning can be used to advantage to direct the course of a catalytic reaction.[22] In the reduction of acid chlorides, for example, it is known that palladium catalyst on a barium carbonate support, suitably poisoned by a preparation of quinoline and sulfur, is very suitable for stopping the process at the aldehyde stage.

3. Selectivity and Specificity.

It is questionable which function of a catalyst is of more importance: its ability to influence the rate of a chemical reaction, or its extreme specificity in influencing one group of reactions and having little or no effect on others. This ability to affect certain specific reactions and not others can be utilized in a selective sense. A given catalyst may stimulate the modification of one functional portion of a molecule and yet have no effect upon other portions. Thus, aluminum isopropoxide will catalyze the reduction of a carbonyl group to an alcohol group without

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[22]Ibid., pp. 354-358

affecting a C - C double bond in the same molecule.[23]

Although the question of which effect, rate variation or selectivity, is of greater importance perhaps cannot be answered, it is obvious that selectivity is a prime factor in determining the catalyst and conditions to use for a given process.

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[23]W. G. Young, W. H. Hartung, and F. S. Crossley, J. Am. Chem. Soc., 58, 100-2 (1936).

III. EXPERIMENTAL

To execute a study of chemical kinetics such as that proposed, numerous factors must be considered. The equipment, materials and procedures must be selected with care in order that the results may have real significance. Other factors, if not studied, must remain constant. The techniques followed in this work have been to a large extent standard, but since they influence so significantly the results obtained, a summary of such techniques is appropriate.

A. Equipment

The reductions carried out in this research employed a standard low-pressure hydrogenation apparatus, manufactured by the Parr Instrument Company of Moline, Illinois. Two modifications in this apparatus were necessary for certain phases of this research. For the temperatures runs carried out to obtain the data for GRAPH II, it was necessary to incorporate a water jacket into the system. For this purpose a water-tight, brass, cylindrical jacket was constructed in this laboratory. It contained the reaction bottle and permitted circulation of water around the bottle by a centrifugal water pump to and from a large reservoir. This jacket replaced the metal shield of the Parr equipment.

In addition, for hydrogenations in which the total initial hydrogen pressure was about 16 p.s.i., the regular Parr pressure gauge was replaced by a mercury manometer.

B. Materials

1. Preparation of Catalyst.

One phase of this research has consisted of a study of the effect of catalyst sample upon the rate of hydrogenation. For this purpose several samples of catalyst were prepared from chloroplatinic acid by the procedure outlined by Adams, Voorhees, and Shriner.[1] For most of the remainder of this research, however, a catalyst prepared by the American Platinum Works was used.

2. Hydrogen.

Hydrogen for this entire work was taken from a cylinder produced by the National Cylinder Gas Company. It was used without further purification.

3. Quinoline.

In these investigations Eastman Kodak white label synthetic quinoline was used after careful purification. It was first allowed to stand over sodium hydroxide pellets for three weeks or more, decanted and distilled through a six-foot Vigreux column. The fraction boiling at a constant temperature of 234.5° C at 740 mm (corrected) was collected.[2]

Upon comparing rate constants for the hydrogenation of quinoline purified by the procedure outlined above, it was evident that some modifications in the procedure were necessary. Two samples of quinoline

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[1]R. Adams, V. Voorhees, and R. L. Shriner, Organic Syntheses, Collective Volume I (New York: John Wiley and Sons, Inc., 1932), p. 463.

[2]Anschütz thermometers were used consistently in the distillation work without further correction.

purified in the same manner did not necessarily hydrogenate at the same rate. In order to eliminate the possibility of oxygen and moisture contamination, the quinoline was redistilled in an atmosphere of nitrogen,[3] and maintained in this condition in all subsequent handling until it was hydrogenated. It was found necessary to pass the nitrogen through a glass wool filter to remove small particles, presumably charcoal. The experimental evidence which led to these modifications is indicated in TABLE I, p. 28.

[3]National Cylinder Gas Company.

TABLE I[4]

Effect of Employing an Atmosphere of Nitrogen

Catalyst APWI 0.2000 gram. 0.02 Mole Quinoline

Hydrogenation Number	Quinoline Sample	$K_I^o \times 10^4$	Atmosphere
30	14 IV	158	air
32	14 III	150	air
39	75 I	124	air
56	99	121	nitrogen (unfiltered)
68	114	167	nitrogen (unfiltered)
72	120	147	nitrogen (unfiltered)
83	122	180	nitrogen (filtered)
90	136	190	nitrogen (filtered)

[4]In this table, "Hydrogenation Number" indicates the order in which the runs referred to occurred in the research. The notation under "Quinoline Sample" is arbitrary and refers to the original laboratory notes. The corrected constant, $K_I^o \times 10^4$, is defined on p. 33. For the constants listed above and for all others cited in this work, the factor of hydrogen volume has not been compensated for. This is satisfactory for the purposes of this investigation, since the hydrogen volume is constant. To obtain a true constant for the hydrogenation of quinoline, however, rate constants cited here as K_I^o must be multiplied by a factor of 4.43, the volume of the system employed.

TABLE II

Effect of Acetic Acid

Quinoline Number 136 0.02 Mole

Catalyst Number APNI 0.2000 gms.

Saturated with	Hydrogenation Number	$K_I^o \times 10^4$
Air	92	188
Air	97	176
Nitrogen	102	186
Nitrogen	104	179

4. Acetic Acid.

The acetic acid used as a solvent in this work was produced by General Chemical Company, guaranteed to be 99.5% pure. It was further purified by distillation through a five-foot helix-packed column, the portion boiling at a constant temperature of 115.8° C at 740 mm was considered to be sufficiently pure.

Displacement of the dissolved air in the acetic acid purified in this manner was performed by bubbling nitrogen through it for 2-3 hours. The product showed no appreciable variation from that containing air, as is indicated in TABLE II, p. 29.

C. Procedure

1. Measurement of Materials.

The samples of catalyst and benzoic acid, used as catalyst standard, were weighed on an analytical balance to an accuracy of ± 0.0002. The hydrogen pressures were read to an accuracy of approximately ± 0.1 pound on the Parr gauge and to a greater accuracy on the manometer. Samples of quinoline ranging from 0.01 to 0.06 mole were measured by means of a calibrated pipette. Suitable connections permitted carrying out these measurements in an atmosphere of nitrogen. In all hydrogenations carried out, 50.0 mls. of acetic acid was used, measured in a 100 ml. cylinder.

2. Hydrogenation Procedure.

A sample either of quinoline or benzoic acid was measured accurately and placed in a hydrogenation bottle with the acetic acid and the catalyst portion. The bottle was then inserted in the apparatus and alternately

evacuated to the boiling point of acetic acid and compressed with 30-50 pounds pressure of hydrogen. This operation was repeated three times in each case. The rate of reaction was measured by recording the pressure drop as a function of time, the time interval being determined with a precision stop watch.

With hydrogenation runs carried out in the water jacket at constant temperature, this procedure was modified slightly. The acetic acid was first placed in the bottle and allowed to come to the temperature of the bath. Then the hydrogen acceptor and the catalyst were added and the regular procedure followed.

3. Isolation of Products.

After the reduction was stopped, the reaction mixture was filtered to recover the spent catalyst. In those cases in which the hydrogenation product was to be analyzed, the acetic acid was distilled off in a distilling flask, the product rendered basic with alkali, and extracted with benzene. It was finally distilled through a fractionating column, in some cases under atmospheric pressure and in others under reduced pressure.

IV. DISCUSSION OF RESULTS

A. Determination of Rate Constant

1. Introduction.

In any kinetic study, the most difficult problem is recognizing and controlling all of the variables which may influence the rate of the reaction. Actually the quality of the work is measured by the completeness with which this problem has been solved. As a method of recording results in work of this kind, the influence these variables have is commonly expressed in terms of the changes they make in the reaction rate constant.

The ideal method of conducting a kinetic study would be to consider each of the variables one at a time, keeping all others constant. From an experimental standpoint, however, it may be difficult if not impossible to do this. Furthermore, it is sometimes convenient to express the results for conditions different from those used in the experimentation. These difficulties may be overcome by adopting a series of standard conditions, and by devising means for correcting results obtained under other conditions to the arbitrarily adopted standards.

Defining standard conditions, however, is only a partial solution to the problem of interpretation. In order to analyze the experimental results of a kinetic study in a reasonable and consistent fashion, a formalism to serve as a basis of interpretation must be adopted and adhered to rigidly. Modifications must be made only when evidence clearly indicates the need. On the basis of previous work and certain preliminary runs made with quinoline, a formalism was set up. The significance

of the provisions in this formalism is made clear by reference to a sample hydrogenation. GRAPH I represents the data of Hydrogenation Number 70. The decrease in the logarithm of the pressure as ordinate is plotted against the time as abscissa.

2. Formalism for the Interpretation.

The factors considered in the formalism serving as the basis of interpretation are outlined below for the purpose of an overall picture. The individual factors will be considered in more detail in the following section.

a. In the work on the benzene nucleus a standard catalyst was defined as one whose rate constant for the hydrogenation of benzoic acid was 250 x 10^{-4} reciprocal minutes, for one gram of catalyst at 30° C in 50 mls. of acetic acid under an initial hydrogen pressure of 64 pounds per square inch. Similarly, a standard reaction rate constant of a reaction, designated as K_I^o, was defined as the rate constant of a given reaction corrected to 30° C and one gram of catalyst, and multiplied by a "catalyst factor" to bring all catalysts to the same basis.[1]

b. On plots such as illustrated by GRAPH I, initial points (1-3 minutes) were attributed to reduction of the catalyst from platinic oxide to some mixture of platinum and platinum oxides, which actually serves as the catalyst.

c. A break which seemed to occur approximately at the point of addition of two moles of hydrogen per mole of quinoline was attributed

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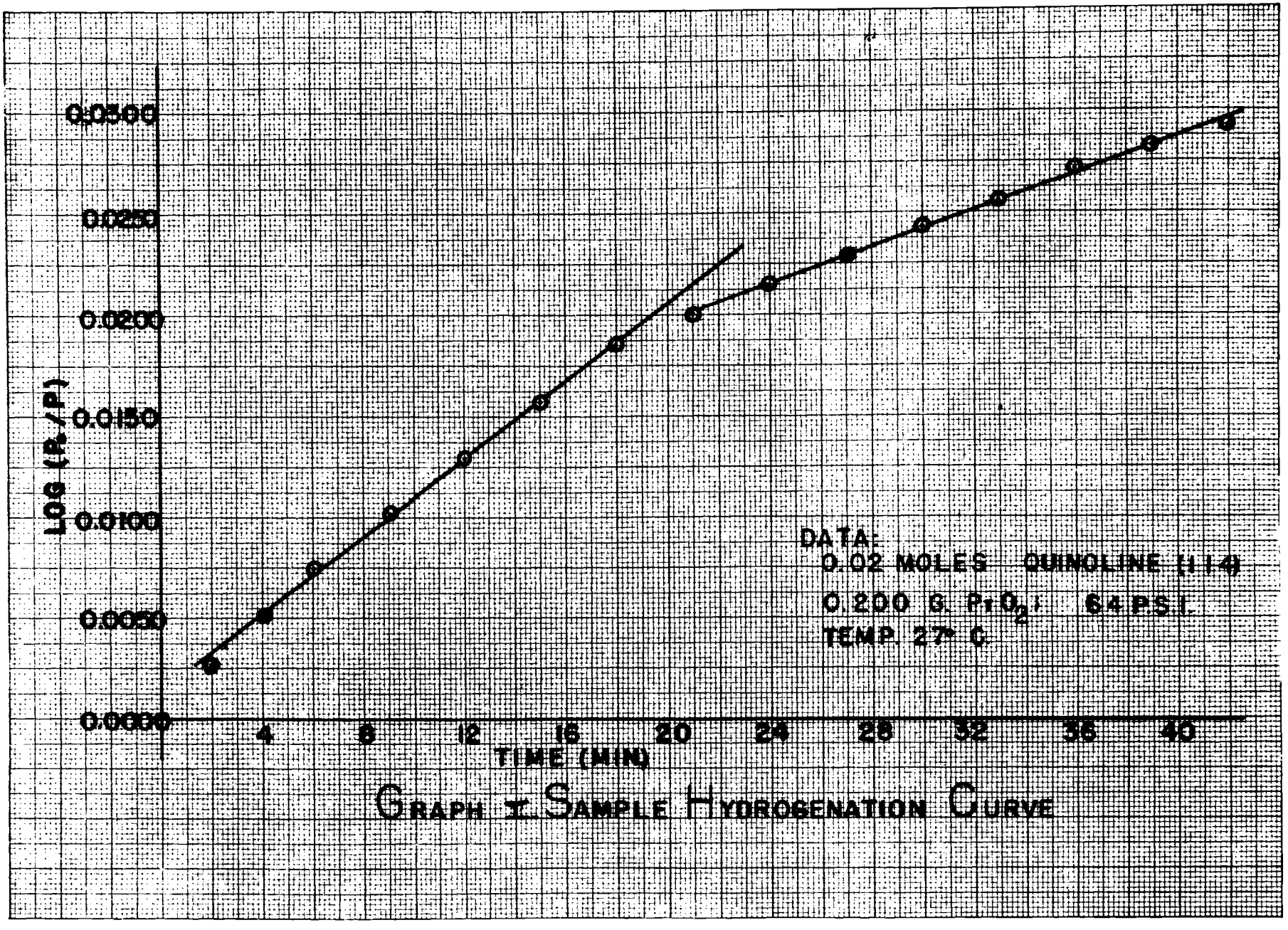
[1]H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., 67, 272-276 (1945).



GRAPH I. SAMPLE HYDROGENATION CURVE

to a fundamental change in the rate. Such transition points are seldom sharply defined, so points on the plot immediately before and after the break were considered questionable.

d. An induction period was postulated in many cases for a short interval after the initial break in slope.

e. Eventual tapering off of the rate of reduction with time was believed to be poisoning. This seemed particularly justifiable when it was observed to occur after a time interval similar to that at which benzoic acid poisoned. In all cases a sufficient number of unpoisoned and otherwise satisfactory runs were noted to guarantee that this sloping off was not due to a change in rate or order.

3. The Standard Reaction Rate Constant.

From a logarithmic plot such as GRAPH I, it is possible to determine immediately whether or not the reaction is first order with respect to hydrogen pressure, one or more straight lines indicating such an order. By equation (13), p. 8, the slope of such a line or lines may be used to calculate a reaction rate constant for the hydrogenation under the conditions of the experiment. These conditions will vary slightly from one experiment to the next. But in order to make a kinetic study of these results, the conditions for which the results are reported must be the same.

As pointed out in the Introduction, p. 32 above, the difficulty caused by these varying factors may be overcome at least in part by defining certain standard conditions, and correcting all results to these conditions. For this purpose it was found useful in the work on the benzene nucleus to define a standard catalyst and a standard reaction rate

constant in the manner expressed above. The standard catalyst was defined in order that all catalysts could be referred to the same standard. The standard reaction rate constant was defined in order that all other variables could be referred to the same standard. It was not necessary to correct for acetic acid volume and initial hydrogen pressure, since these factors remained constant throughout the work. The subscript I on the standard reaction rate constant indicates that for a given hydrogenation the constant recorded is for the first step in the hydrogenation process. The subscript II indicates values of the rate constant for the second step (see TABLE IV, p. 43).

Using the definition of a standard catalyst, a catalyst factor was obtained for each catalyst. This was done by dividing 250×10^{-4} by the experimentally determined rate constant for the hydrogenation of benzoic acid. The catalyst factors for the various catalysts used in this work are tabulated in TABLE III, p. 37.

Benzoic acid was arbitrarily selected as standard hydrogen acceptor for a number of reasons: it could be obtained in a high degree of purity; it supplied a benzene nucleus; its rate of hydrogenation was zero order with respect to its concentration; its rate was sufficiently fast to fall within a range of reasonable observing accuracy with the Parr equipment.

The standard reaction rate constant implies the standardization of the factors: acetic acid volume, initial hydrogen pressure, amount of catalyst, and temperature. The volume of acetic acid in which the benzoic acid or quinoline was dissolved was held constant throughout the work. In all runs reported in this thesis the initial hydrogen pressure was set at about 64 pounds per square inch. In all runs except those

TABLE III

Catalyst Factor

Catalyst Sample	$K_{30.0^{o}}$ C/gram x 10^{-4} for Benzoic Acid	Catalyst Factor
16	223	1.12
36	180	1.39
49	207	1.21
APWI	192	1.30

studying the effect of amount of catalyst, 0.2000 gram of catalyst was employed and a factor applied in order to interpret the results on the basis of 1.0000 gram of catalyst. Finally, for the conversion of rate constants at temperatures other than 30° C to standard temperature, a determination was made of the activation energy, equation (18), p. 11, being employed.

4. Energy of Activation.

Determination of the energy of activation and its use in equation (23), p. 13, constitute the means whereby a reaction rate constant may be corrected to temperatures other than that at which the reaction is carried out. The need for such a means has been shown -- without it, correlation of results becomes only approximate and a kinetic study impossible. GRAPH II represents the results of such a determination. The reaction rate constant was determined at the temperatures 17° C, 23° C, 28° C, and 35° C. (The points corresponding to 41° C and 45° C will be considered in Part E of this division.) By equation (18), p. 11, the slope of the line in this graph is equal to the energy of activation divided by 2.303 R. Therefore, by multiplying the observed slope by this factor, a value of 6300 calories was obtained for E_a.

Inserting this value into equation (23), p. 13, an expression is obtained from which the reaction rate constant at any desired temperature may be calculated, knowing the reaction rate constant at some one temperature. Or, as is usually done, the reaction rate constant at the temperature of a given reaction may be corrected to a standard temperature, e.g. 30° C. This equation is valid, of course, only within the range in

GRAPH II LOG K VS $\frac{1}{T}$.

which the E_a is valid.

In practice a plot is frequently made of Δ log K against temperature, by employing equation (23), p. 13. Δ log K is first calculated at several temperatures (e.g., 20, 25, 30, 35° C) for a one degree increment of temperature. Plotting these results against temperature and drawing a smooth curve through these points gives a graph from which the rate of change of log K per degree may be read directly at any desired temperature.

5. Sample Calculation of a Reaction Rate Constant.

The analysis of the results of a kinetic investigation of catalytic hydrogenation begins necessarily with the calculation of reaction rate constants. Data on the rate of decrease of pressure is first plotted as in GRAPH I. The existence of what are apparently two lines indicate that the reaction probably occurs as a two-step process, and that each step is first order with respect to hydrogen pressure. From the slopes of the lines values can be calculated for the reaction rate constants, which were then corrected to one gram of catalyst, 30° C and benzoic acid standard. The calculation for Hydrogenation Number 70 (GRAPH I) is as follows:

Slope to the break point, m_I	=	9.32×10^{-4}
$(2.303)(m_I) = K_{26.4^\circ C}$/0.2000 gram catalyst	=	21.5×10^{-4}
$K_{26.4^\circ C}$/gram catalyst	=	$107. \times 10^{-4}$
log K/°C at 26.4° C (from GRAPH II)	=	0.01514 /° C
log K/ 3.6° C at 26.4° C	=	0.0545 /° C
$K_{30.0^\circ C}$/gram catalyst	=	$121. \times 10^{-4}$

Catalyst Factor for Catalyst APWI	=	1.30
K_I^o	=	$158. \times 10^{-4}$

Slope of second line, m_{II}	=	4.17×10^{-4}
$K_{27.4^\circ C}$/ 0.2000 gram catalyst	=	9.59×10^{-4}
$K_{27.4^\circ C}$/ 1.0000 gram catalyst	=	48.0×10^{-4}
log K/ $^\circ$ C at 27.4° C	=	0.01503 /$^\circ$ C
log K/ 2.6° C at 27.4° C	=	0.0391/2.6°C
$K_{30.0^\circ C}$/ 1.0000 gram catalyst	=	52.5×10^{-4}
K_{II}^o	=	68.2×10^{-4}

6. Procedure for Investigation

In each hydrogenation run the rate constant for the first and frequently the second steps were calculated in the manner outlined above. Then, to study, for example, the effect of particular catalyst preparation upon the rate of hydrogenation, the values obtained for the rate constants in a series of hydrogenations were compared and differences as well as general trends noted.

In this manner the following factors and their effect upon the rate constant were studied: nature and amount of catalyst, nature and amount of quinoline, and temperature. The results obtained from each will be discussed in some detail.

B. Factors Influencing the Rate Constant

1. Nature of Catalyst.

It has been found that the nature of the catalyst, determined to a large extent by the conditions of its preparation, profoundly affects the value obtained for a rate constant. This effect is illustrated in TABLE IV, p. 43.

Several conclusions may be drawn from the data of TABLE IV:

a. Other conditions being the same, two catalyst preparations will in general reduce quinoline at two different rates.

b. A catalyst factor based upon benzoic acid as standard is not suitable for correcting to the same standard various values of K_I obtained with different catalyst preparations. Such a factor is suitable for correcting values of K_{II}. These facts are taken as evidence for a two-step hydrogenation process in which the pyridine nucleus is hydrogenated first.

c. Not only is the pyridine nucleus hydrogenated first in preference to the benzene nucleus, but also at a faster rate. Therefore, it is reasonable to expect that a catalyst sample which reduced one nucleus at a faster rate than a second catalyst, might well reduce the other nucleus at a slower rate. This effect was observed in a number of hydrogenations and is illustrated in TABLE IV by the first two runs cited, in which values are given for K_I and K_{II}.

d. The lack of correlation between supposedly "corrected" values of the rate constant for the first stage of the hydrogenation indicates that a nucleus more nearly like that being attacked would perhaps be more

TABLE IV

Effect of Catalyst Sample Upon the Rate Constant

0.04 Mole Quinoline

Catalyst Sample	Quinoline Sample	$K_I \times 10^4$	$K_I^o \times 10^4$	$K_{II} \times 10^4$	$K_{II}^o \times 10^4$
16 (0.2000 gram catalyst)	14 III	194	212	52.0	58.2
36 (0.2000 gram catalyst)	14 III	257	358	39.3	54.7
36 (0.1000 gram catalyst)	14 IV	277	385	- (poisoned)	-
49 (0.1000 gram catalyst)	14 IV	201	243	- (poisoned)	-

satisfactory as a standard. Pyridine would be the logical possibility, but time has not permitted investigation of its applicability.

The reasons for the variations in catalysts toward the hydrogenation of benzoic acid (TABLE III) and of quinoline (TABLE IV) probably involve several factors. Surface area, particle size and active centers on the catalytic surface must be considered in any attempt to define these factors. However, another effect has been shown to be involved, which could influence the rate of hydrogenation appreciably. Materials other than platinum have been shown to be present in the catalysts by qualitative spectrographic analysis. TABLE V outlines the result of this analysis.

A correlation may well exist between the elemental constituents of the several catalysts and their varying abilities to reduce benzoic acid and quinoline. Catalyst 36, e.g., was a remarkably powerful catalyst for the reduction of quinoline, and was the only one to show the presence of manganese and boron under analysis. Catalysts 49 and APWI were of the same order of effectiveness as catalysts; both were seen to contain traces of magnesium and relatively large amounts (probably 0.1 - 3%) of palladium. However, it is certainly not justifiable to attribute all differences in catalysts to dissimilarities in chemical composition, since it is known that factors such as particle size are of considerable significance. Some additional observations and considerations will be treated in Part E of this division.

TABLE V

Qualitative Spectrographic Analysis[a]

Catalyst Sample	Elements Found
16	Si,[b] Ca[c]
36	Si,[b] B,[b] Mn
49	Mg,[c] Pd
APWI	Mg,[c] Pd, Ca,[b] Ag[d]

[a]Spectrograms for the catalyst samples were prepared by Dr. W. M. Spicer, Professor in the School of Chemistry, Georgia Institute of Technology.

[b]The elements frequently found in glass were reported as trace impurities by R. Adams and R. L. Shriner, J. Am. Chem. Soc., 45, 2174-5 (1923).

[c]These elements are classed as doubtful, since their contamination of samples has been noted in previous spectrographic investigations.

[d]Catalysts 16, 36, and 49 were prepared from C. P. chloroplatinic acid, and catalyst APWI was purchased from the American Platinum Works.

2. Amount of Catalyst.

The nature of the catalyst has been shown to have a large and unpredictable effect upon the rate of reaction, both by considerations of the nature and action of the catalyst and by experimental evidence. The effect of the amount of catalyst, on the other hand, is seen to be relatively simple and straightforward.

The action of a catalyst in a heterogeneous reaction is known to be directly related to the surface area of the catalyst, and, in particular, to the number of active centers on the catalytic surface. It would follow from this statement that so long as sufficient hydrogen acceptor were present, increasing the amount of a given catalyst should increase the rate of hydrogenation proportionally. The results of a limited investigation of this question are outlined in TABLE VI, p. 47.

The results of Hydrogenation Numbers 105 and 106 are exactly as predicted. The rate of hydrogenation was directly proportional to the amount of catalyst. The reason for the variation in the case of Hydrogenation Number 107 is not clear. From the standpoint that it is an isolated run and thus has not been checked, its validity is questionable. However, an increase in rate less than that expected by direct proportionality, as was observed in this case, has some a priori justification. When the concentration of quinoline is small compared with the amount of catalyst present, there may well be a competition for catalyst surface between quinoline and the tetrahydroquinoline formed. Tetrahydroquinoline is believed to hydrogenate at a much slower rate than quinoline (see Part E below), so a competition of this sort would tend to lower the calculated value of the rate constant. Further evidence of this competition was

TABLE VI

Effect of Amount of Catalyst on the

Reaction Rate Constant

0.02 Mole Quinoline (136) Catalyst APWI.

Hydrogenation Number	Amount of Catalyst	$K_{30.0/\text{ x gram}} \times 10^4$	$K_I^o \times 10^4$
106	0.1000 gram	14.4	187
105	0.2000 gram	28.7	187
107	0.4000 gram	48.4	157

noted when it was observed in this particular hydrogenation (Number 107) that the slope dropped off appreciably before two molecules of hydrogen per molecule of quinoline had been consumed. Thus it may be presumed that the competition became more noticeable when the concentration of tetrahydroquinoline became relatively large.

However, from a poisoning standpoint, the observed decrease in K_I^o would not have been anticipated. If any catalyst poison were introduced through the quinoline, the acetic acid, the hydrogen or the reaction vessel, its slowing influence would have greater effect on the calculated rate in the case of 0.1000 gram of catalyst than in the larger quantities. A more or less fixed amount of poison would be present with a larger amount of catalyst. On the whole the consideration of this phase is unduly complicated by a lack of data.

3. Nature of Quinoline.

The most complicating factor in this entire investigation has been not that different catalyst samples prepared in a similar fashion hydrogenated quinoline at different rates, but that different quinoline samples, purified in exactly the same fashion, also hydrogenated at different rates. Evidence of this variation was cited in TABLE I, p. 28.

Distillation of quinoline in an atmosphere of nitrogen and maintaining it under such an atmosphere was partially successful. Here again, however, small changes were noted over a period of time which could not be explained readily.

As noted before, the variables of moisture and oxygen were suspected. Two series of experiments were carried out in an attempt to solve this

problem, but little success was encountered mainly because the treatment of the quinoline itself was not quite satisfactory. When parallel runs were made over a period of time with two portions of a sample of quinoline, one exposed to air and the other not, the reaction rate constants calculated for each increased to a reasonably constant value. The exposed portion was hydrogenated at the faster rate.

In a second series of runs this investigation was repeated with quinoline that had been distilled in an atmosphere of nitrogen and kept in such an atmosphere for several days in the dark. In this case the rate constant for the unexposed portion remained constant, but that for the exposed portion decreased somewhat with time.

These results indicate primarily that special care must be exercised in purifying, storing, and handling the quinoline. For this research the quinoline was kept in bottles large compared with the volume of quinoline stored, nitrogen being kept above it. Since this procedure has not given completely satisfactory results, modification in future work would probably be in order. Storing the quinoline in smaller vials in the dark would be a logical procedure to try.

4. Concentration of Quinoline.

It was observed with benzoic acid and with pyridine that the rate constant of the hydrogenation was zero order with respect to concentration of hydrogen acceptor. Such has also been found to be the case with quinoline over a range of concentrations of 0.01 to 0.06 mole. The experimental evidence substantiating this conclusion is indicated in TABLE VII, p. 50.

TABLE VII

Quinoline (77III) Catalyst APWI 0.2000 gram.

Hydrogenation Number	Concentration of Quinoline	$K_I^o \times 10^4$
47	0.01 mole	121
40	0.02 mole	125
46	0.03 mole	126
43	0.04 mole	124
42	0.06 mole	124

C. Product of Hydrogenation

In the temperature range considered in this investigation (17 - 37° C), results such as that illustrated by GRAPH I, p. 34, indicate that some phase of the hydrogenation process ends with the addition of two molecules of hydrogen to one molecule of quinoline. In order to isolate and identify the product of this step in the reduction, several runs were stopped when the pressure drop corresponded to this point. The catalyst and acetic acid were removed according to the procedure discussed previously and the product distilled. The portions distilling from 246.4 - 246.6° C at 736 mm (corrected) were collected in fractions. The boiling point of tetrahydroquinoline is taken to be 251° C at 760 mm. To establish further the identity of this compound, the hydrochloride was prepared and found to melt at 181° C (uncorrected). The melting point of the hydrochloride of tetrahydroquinoline is taken to be 180 - 181° C.[2] Other possible products of the hydrogenation will be considered under Part E, p. 62.

D. Mechanism of Hydrogenation

1. Introduction.

Although some data will be considered for the processes of going from quinoline to decahydroquinoline under the conditions of this experiment, and going from quinoline to what may be dihydroquinoline at temperatures greater than 37° C (Part E), the data of this investigation

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[2]Characterized by S. O. Winthrop and E. L. Pollitzer, Georgia Institute of Technology.

deals largely with the hydrogenation of quinoline to tetrahydroquinoline. Therefore, the analysis of this data in terms of reaction mechanism will be limited to this latter reaction.

From a consideration merely of the physical and chemical properties of the reactants and products of the hydrogenation there are many possible mechanisms for the reaction being considered. A complete derivation of the rate expressions for each of these would be unreasonably long to include at this point. For the purpose of conciseness, therefore, a sample calculation will be included, illustrating the method, and the overall presentation will be limited to a listing of the results that may be obtained by applying the method to other possible mechanisms. In each case it is assumed that the adsorption and activation processes and the reaction and desorption processes each occur as one step. The former assumption is merely a matter of the definition of activation. The latter assumption is believed to be justified since the reaction does not stop with the formation of tetrahydroquinoline. Failure of this material to desorb rapidly compared to the rate at which it is formed would necessitate a one-step reaction, a condition which GRAPH I, p. 34, does not substantiate.

2. Possible Mechanisms and their Rate Expressions.

Three general cases will be considered: the organic reactant is adsorbed and activated and the hydrogen not; the hydrogen adsorbed and activated and the organic reactant not; both the hydrogen and the organic reactant adsorbed and activated. The notation used in this discussion is as follows:

Q-	quinoline
H_2-	hydrogen
Qx-	activated quinoline
Hx-	activated hydrogen (one molecule)
QHx-	quinoline and one molecule of hydrogen, both activated
HHx-	two molecules of hydrogen, both activated
QHHx-	quinoline and two molecules of hydrogen, all activated
DHQ-	dihydroquinoline
DHQx-	activated dihydroquinoline
DHHQx-	dihydroquinoline and one molecule of hydrogen, both activated
THQ-	tetrahydroquinoline
k_i-	a conventional rate constant
k_{-i}-	the rate constant for the reverse of the reaction associated with k_i
( )	denotes concentration
(catalyst)	denotes amount of catalyst, concentration not being applicable.

a. Case I. Organic reactant is adsorbed and hydrogen not.

1. Mechanism:

$$Q + \text{Catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Qx \qquad (1a)$$

$$Qx + 2\ H_2 \xrightarrow{k_2} THQ + \text{Catalyst} \qquad (1b)$$

Assuming a constant concentration of (Qx)[3] and the irreversibility of equation (2) in the temperature range taken, and considering a material balance about it (i.e., the amount formed in a unit time equated to the amount decomposed in the same time interval),

$$k_i\ (Q)\ (\text{Catalyst}) = k_{-1}\ (Qx) + k_2\ (Qx)\ (H_2)^2. \qquad (1c)$$

Therefore,

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[3]It is important to note that this assumption will be applied to any activated state (Ax) in the derivation of later expressions.

$$(Qx) = \frac{k_1 (Q) (\text{Catalyst})}{k_{-1} + k_2 (H_2)^2} . \qquad (1d)$$

The overall rate of the reaction can be expressed:

$$\frac{d (THQ)}{dt} = k_2 (Qx) (H_2)^2. \qquad (1e)$$

Combining equations (4) and (5), a rate expression is obtained:

$$\frac{d (THQ)}{dt} = \frac{k_1 k_2 (\text{Catalyst}) (Q) (H_2)^2}{k_{-1} + k_2 (H_2)^2} . \qquad (1f)$$

2. Mechanism:

$$Q + \text{Catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Qx \qquad (2a)$$

$$Qx + \text{Hydrogen} \xrightarrow{k_2} DHQ + \text{Catalyst} \qquad (2b)$$

$$DHQ + \text{Catalyst} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} DHQx \qquad (2c)$$

$$DHQx + H_2 \xrightarrow{k_4} THQ + \text{Catalyst} \qquad (2d)$$

Rate Expression:

$$\frac{d\cdot(THQ)}{dt} = \frac{k_1 k_2 (H_2) (Q) (\text{Catalyst})}{k_{-1} + k_2 (H_2)} . \qquad (2e)$$

Case II. Hydrogen adsorbed and activated and organic reactants not.

1. Mechanism:

$$2\ H_2 + \text{Catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ Hx \qquad (3a)$$

$$2\ Hx + Q \xrightarrow{k_2} THQ + \text{Catalyst} \qquad (3b)$$

Rate Expression: (material balance taken about 2 Hx)

$$\frac{d\,(THQ)}{dt} = \frac{k_1\, k_2\, (Q)\, (H_2)^2\, (\text{Catalyst})}{k_1 + k_2\, (Q)} . \qquad (3c)$$

2. Mechanism:

$$H_2 + \text{Catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hx \qquad (4a)$$

$$Hx + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HHx \qquad (4b)$$

$$HHx + Q \xrightarrow{k_3} THQ + \text{Catalyst} \qquad (4c)$$

Rate Expression:

$$\frac{d\,(THQ)}{dt} = \frac{k_1\, k_2\, k_3\, (H_2)^2\, (Q)\, (\text{Catalyst})}{k_{-1}\, k_{-2} + k_{-1}\, k_3\, (Q) + k_2\, k_3\, (H_2)\, (Q)} . \qquad (4d)$$

Case III. Both hydrogen and organic reactant adsorbed and activated. Due to the complexity of the derivative of the rate expressions from the mechanisms in this case, it was necessary to simplify the various steps as they occurred. Consequently, the rate expressions finally derived were already in a simplified form. To avoid repetition these expressions will not be recorded here but will be listed in the following section under Simplified Rate Expressions.

1. Mechanism:

$$Q + \text{Catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Qx \qquad (5a)$$

$$Qx + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} QHx \qquad (5b)$$

$$H_2 + \text{Catalyst} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Hx \qquad (5c)$$

$$Hx + Q \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} QHx \qquad (5d)$$

$$QHx + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} QHHx \qquad (5e)$$

$$Hx + H_2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} HHx \qquad (5f)$$

$$HHx + Q \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} QHHx \qquad (5g)$$

$$QHHx \xrightarrow{k_8} THQ + \text{Catalyst} \qquad (5h)$$

2. Mechanism:

$$H_2 + \text{Catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hx \qquad (6a)$$

$$Hx + Q \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} QHx \qquad (6b)$$

$$Q + \text{Catalyst} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Qx \qquad (6c)$$

$$Qx + H_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} QHx \qquad (6d)$$

$$QHx \overset{k_5}{\rightarrow} DHQ + \text{Catalyst} \qquad (6e)$$

$$DHQ + \text{Catalyst} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} DHQx \qquad (6f)$$

$$DHQx + H_2 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} DHHQx \qquad (6g)$$

$$DHHQx \overset{k_8}{\rightarrow} THQ + \text{Catalyst} \qquad (6h)$$

4. Analysis of Mechanisms.

The rate expressions listed above may be simplified somewhat by making a number of assumptions. Certain of these assumptions are eminently reasonable and will be applied to all rate expressions. They are listed below. In the case of some others, however, there is reason to question their validity and general applicability, so they will be indicated when applied.

a. Assumptions.

1. The rate of adsorption and activation of hydrogen is greater than that of the organic reactants;

2. The rate of deactivation and desorption of unreacted reactants is small in comparison to the rate of adsorption and activation of hydrogen and organic reactants;

3. Terms containing the product of rates known to be relatively small can be neglected.

b. Simplified Rate Expressions. Assumptions Made

Case I.

1. $\frac{d(THQ)}{dt} = k_1 (Q) (Catalyst)$ $k_{-1} \ll k_2$ (7a)

2. $\frac{d(THQ)}{dt} = k_1 (Q) (Catalyst)$ $k_{-1} \ll k_2$ (7b)

Case II.

1. $\frac{d(THQ)}{dt} = k_1 (H_2)^2 (Catalyst)$ $k_{-1} \ll k_2$ (8a)

2. $\frac{d(THQ)}{dt} = k_1 (H_2) (Catalyst)$ $k_{-1} \ll k_2$ (8b)

Case III.

1. $\frac{d(THQ)}{dt} = (Catalyst) \left[k_1 (Q) + k_3 (H_2)\right]$. (9)

Assuming: Terms containing rates of deactivation and desorption of unreacted materials are small compared to terms not containing such rates.

Case III.

2. $\frac{d(THQ)}{dt} = (Catalyst) \left[k_1 (H_2) + k_3 (Q)\right]$. (10)

Assuming: $k_{-3} \ll k_4 (Q)$

$k_{-1} \ll k_2 (H_2)$

$k_{-2} + k_{-4} \ll k_5$

$k_{-2} \ll k_4 k_5 (Q)$

$k_{-4} \ll k_2 k_5 (H_2)$

c. Application of Experimental Data. It was shown in Part B of this division that:

1. The hydrogenation of quinoline to tetrahydroquinoline occurs as a single step in the temperature range 17 - 37° C;

2. The rate of hydrogenation is zero order with respect to the concentration of hydrogen acceptor;

3. The rate is first order with respect to hydrogen pressure;

4. The rate is directly proportional to the amount of catalyst used;

5. For a given catalyst the rate is different in general from the rate at which benzoic acid is reduced.

These experimental facts may be applied to a consideration of the proposed reaction mechanisms, and some conclusions may be drawn.

Case I of the proposed mechanisms may be ruled out of consideration by (2) above. Similarly, Number 1 of Case II is eliminated by (3) above. Number 2 of Case II meets the specifications of (2) and (3), but it is invalid on the basis of (5) above. By merely making the assumptions noted on p. 58, the rate expression of Number 2 becomes independent of the rate of adsorption of hydrogen acceptor. It would follow from this statement that all hydrogen acceptors of equal purity would hydrogenate at the same rate. On the basis of all the vast amount of catalytic work which has

been carried out with platinum oxide and other catalysts, this conclusion is not justified. Therefore, both Cases I and II are unsatisfactory as mechanisms of the hydrogenation process.

Mechanism 1 of Case III represents a likely mechanism of the hydrogenation process in that it may be construed to fit all the experimental facts without any questionable assumptions. By merely assuming that the rate of adsorption of pure quinoline on bare catalyst, k_1, is small compared to the rate of adsorption of hydrogen on bare catalyst, k_3, the rate becomes zero order with respect to quinoline concentration and first order with respect to hydrogen concentration. The constants of proportionality is seen to be the rate constant for the adsorption of hydrogen on bare catalyst.

$$\frac{d(THQ)}{dt} = k_3 \text{ (Catalyst) } (H_2). \qquad (11)$$

At first glance it might appear that this expression finally developed to satisfy the experimental data has the same fallacy as Mechanism 2 under Case II above. Thus, it would appear to be independent of the nature of hydrogen acceptor. Proof that this is not the case is shown more readily in terms of Mechanism II, however, since the mathematical expressions are somewhat simpler.

Mechanism 2 of Case III represents an equally acceptable course for the reaction, except that it postulates the formation of dihydroquinoline as an intermediate. There is no experimental evidence to substantiate this postulation in the temperature range of this kinetic investigation.

Again as in Mechanism 1 it might appear that if k_1 (Q) is assumed to be small to meet the experimental observations, the rate becomes mathe-

matically independent of the nature of the hydrogen acceptor. Experimentally this is known to be incorrect. An examination of the postulates underlying the derivation of these expressions reveal that it was assumed that the rates of certain desorption processes are always smaller than the rates of any adsorptive process. Such assumptions are certainly not always valid, for by increasing the complexity of the hydrogen acceptor one decreases its rate of adsorption. The conclusion would be, therefore, that the expressions no longer hold quantitatively as hydrogen acceptors of lower rate of adsorption are considered.

From the fact that k_1 cannot appear in the final rate expressions in both mechanisms 1 and 2, it is concluded that equations (5a) and (5b) are of little importance. Hydrogen apparently adsorbs so much more rapidly upon the catalyst surface than quinoline that quinoline gets little or no opportunity to approach bare catalyst.

E. Additional Notes

The purpose of this investigation as pointed out in the introduction was to make a kinetic study of certain phases of the catalytic hydrogenation of quinoline. Experimental data for such a study was obtained for the hydrogenation of quinoline to tetrahydroquinoline. On the basis of this data mechanisms were proposed for the hydrogenation process. In this work a number of observations were made which were of interest but which were either inclusive or which had no direct bearing on the problem. The more important of these will be mentioned below. In each case additional work is necessary to confirm and interpret the observation.

1. Additional Products of Hydrogenation.

a. Decahydroquinoline. Evidence was cited (p. 51) establishing the fact that tetrahydroquinoline is formed by the reaction of quinoline with two molecules of hydrogen. GRAPH I, p. 34, illustrates the fact observed in every hydrogenation run that the reaction would proceed beyond this point. Several runs were carried to the stopping point, which corresponded to the addition of five molecules of hydrogen to each molecule of quinoline. The only possible product of such an addition would be decahydroquinoline. To substantiate this conclusion an attempt was made to characterize the product, but the procedure used was not that regularly followed. The acidic reaction mixture was filtered and distilled in a Claisen distilling flask. A fraction was collected at 205° C (740 mm), whose odor indicated some decomposition. A picrate derivative was prepared which melted at 195-198° C.

There is some disagreement in the literature as to the configuration

of the compound that should result from this catalytic hydrogenation. Beilstein outlines some early work in which trans-dl-decahydroquinoline was reported by the reduction of quinoline with colloidal platinum in acetic acid medium, and with activated nickel oxide.[4] The melting point of the picrate of trans-decahydroquinoline is listed as 158° C.[5] However, recent work on cis-trans-isomers, fully substantiated, indicates that the cis form is the product of similar hydrogenations in every case.[6] It seems reasonable on the basis of this recent work and of the limited experimental evidence to expect that the decahydroquinoline formed by this catalytic reduction is the cis form.

b. Dihydroquinoline. For all runs made in the temperature range 17 - 37° C the data indicated a one-step process for the formation of tetrahydroquinoline. In determining the energy of activation of this process, hydrogenations were also carried out at 41° C and 45° C. A typical result is shown in GRAPH III, p. 64. In each case there is a possibility of a change in the rate of hydrogenation occurring at a point corresponding to the addition of one molecule of hydrogen to each molecule of quinoline.

In an attempt to isolate any special product of this hydrogenation process, 0.04 mole of quinoline was hydrogenated at 45° C until 0.04 mole of hydrogen had reacted. The base was separated from the acetic acid in

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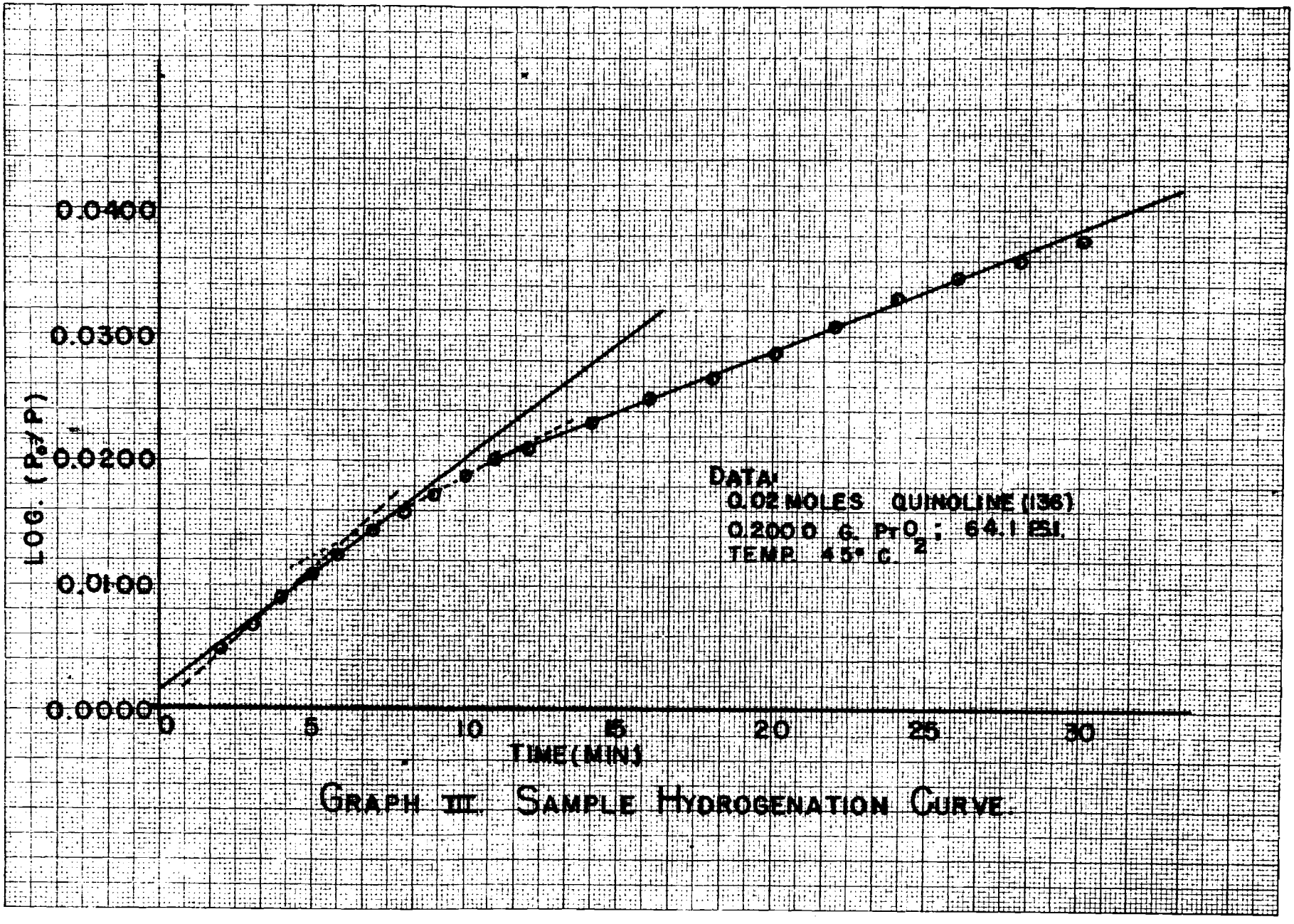
[4]Beilstein's Handbuch der Organischen Chemie, First Supplement, Volume XX (Berlin: Verlag von Julius Springer, 1935), p. 35.

[5]Beilstein's Handbuch der Organischen Chemie, Original, Volume XX (Berlin: Verlag von Julius Springer, 1935) p. 156.

[6]R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, J. Am. Chem. Soc., 64, 1985-2026.



GRAPH III. SAMPLE HYDROGENATION CURVE.

the usual manner (p. 31) and distilled through a 12 inch Vigreux column under a pressure of 5 mm. A fraction was collected between 85° C and 95° C which distilled as a light yellow liquid with an odor similar to that of quinoline. The material present oxidized to a dark liquid in the absence of light more rapidly than was observed with quinoline, tetrahydro- or decahydroquinoline. Since the hydrochloride derivatives of quinoline, tetrahydroquinoline, and decahydroquinoline are recorded in the literature, an attempt was made to prepare this derivative, but a polymer always resulted upon concentrating the solution in the presence of hydrochloric acid. This phenomenon could conceivably be attributed to the vinyl structure which the molecule would possess if the two hydrogens were located on the carbon - nitrogen bond in the pyridine ring. A picrate was prepared and found to melt at 195° C. The corresponding derivative of quinoline melts at 203° C, and that of tetrahydroquinoline melts at 179° C.

No reference to dihydroquinoline has been found in the literature. Several references are noted in Beilstein to dimers and trimers of this compound having unknown structures.[7]

2. Effect of Temperature on Reaction Mechanism.

In Part D of this division two expressions were derived for the mechanism of the hydrogenation of quinoline to tetrahydroquinoline, the first postulated a one-step reaction and the second postulated a two-step reaction through the intermediate formation of dihydroquinoline. Both were seen to explain the experimental data for the temperature range 17 -

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[7]Beilstein, Original, p. 342

37° C. Although no special assumptions were made regarding the rates of equations (5d) - (5h) and (6d) - (6h), it is seen that these do not enter into the rate expressions, equations (9) and (10). Therefore, so long as changing temperature does not alter the validity of those assumptions made in deriving the expressions, they should hold satisfactorily in the higher temperature range, 40 - 45° C.

It has seemed reasonable to try to interpret the results of the hydrogenation of quinoline at elevated temperatures (GRAPH III, p. 64) in terms of these mechanisms. First of all, upon examining GRAPH III it is observed that there are two possible ways of interpreting the results. One can assume that the reaction is a one-step process and that the apparent deviations are systematic errors. Making this assumption, one obtains the first solid line shown in the graph, corresponding to a rate constant (uncorrected for temperature) of 250 reciprocal minutes. On the other hand, one can assume a reaction mechanism corresponding to the formation of dihydroquinoline discussed above. Making this assumption one obtains the two dotted lines shown in the graph, corresponding to the rate constants (again uncorrected), 284 and 214 reciprocal minutes.

It is of particular interest to note where the constants given above for the initial hydrogenation step fall on the plot of log k versus T^{-1} (GRAPH II, p. 39). Those calculated assuming no change in the reaction mechanism do not fall on the line drawn through the points obtained at lower temperatures, whereas those calculated for the addition of the first molecule of hydrogen coincide very well. Therefore, it may be concluded that the experimentally determined rate constants obtained

at "elevated" temperatures for the first step in the hydrogenation give some evidence for the formation of dihydroquinoline as an intermediate in the hydrogenation of quinoline at those temperatures.

Considering the proposed mechanisms themselves, in the lower temperature range there is no reason for favoring Mechanism 2 of Case III over Mechanism 1, p. 57. However, the latter gives no picture of what might be occurring at the first break point in GRAPH III, discussed under "Dihydroquinoline" above. Assuming Mechanism 2, on the other hand, one would merely conclude that at low temperatures k_6, the rate of adsorption and activation of dihydroquinoline, is fast compared with k_4, the rate of adsorption and activation of quinoline, or at least equal to it. At high temperatures k_4 has increased more rapidly with temperature and is greater than k_6. It is important to note that the overall rate of reaction is not affected by these changes, since it is independent of the concentration of hydrogen acceptor. Thus it may reasonably be concluded that there is some evidence favoring a mechanism of the hydrogenation of quinoline postulating the formation of dihydroquinoline in the temperature range 40 - 45° C over a mechanism that does not.

3. The Standard Rate Constant for the Hydrogenation of Tetrahydroquinoline.

Insufficient accurate data has been obtained to decide without question upon a value for the rate constant of the hydrogenation of tetraquinoline to decahydroquinoline, illustrated by Hydrogenation Number 70 as the second line drawn in GRAPH I, p. 34. The chief difficulty lay in poisoning of the catalyst, which occurred in essentially all runs after about 30 - 40 minutes.

However, discarding those runs which obviously poisoned early, an

approximate value of this rate constant was determined to be 60. x 10^{-4} reciprocal minutes.

4. Additional Spectrographic Investigation.

In an attempt to explain why in a group of hydrogenation runs several were observed to be unusually fast, a qualitative spectrographic investigation was made of the spent catalyst samples. It was observed that the metals copper and zinc were present in the catalyst which hydrogenated unusually fast and were not present in the other catalyst. Since these metals are the major constituents of the brass tube leading into the hydrogenation bottle, it was concluded that special care need be exerted in cleaning this tube before each hydrogenation. The practice employed previously of rinsing with methyl alcohol and drying by use of an aspirator is perhaps not completely satisfactory.

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